

Characterization of $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ Thin Films Prepared by Pulsed Laser Deposition

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ABSTRACT

A pulsed laser deposition system was employed to fabricate thin films of $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ solid electrolyte. The deposition process was carried out at room-temperature, resulting in amorphous films. These as-deposited films had a large optical band gap of 5.13 eV, and exhibited a lithium-ion conductivity of 3.35×10^{-7} S/cm. The films were then annealed, and the effect of annealing on the optical and electrical properties of the films was examined. After annealing at 1000 °C, the films were found to be cubic with a narrower band gap of 3.64 eV. In addition, these annealed films showed an inferior ionic conductivity than the as-deposited ones.

INTRODUCTION

Solid state micro-batteries have been under investigation for decades for usage in micro robotics (micro-electromechanical systems) and wireless sensors, etc [1]. A lot of good work has been done to enhance the overall performance of the micro batteries [2-5]. The main strategies have been aimed at improving the quality of the electrolyte and the compatibility between the electrolyte and electrode. A good electrolyte should have high ionic conductivity, large band gap, and wide electrolyte window that matches well with electrode work functions [6]. On the other hand, the electrolyte should have good chemical stability against moisture and be suitable for fabrication as a dense membrane [6, 7].

A newly developed electrolyte material of bulk $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ (LLZO) was found to have not only high ionic conductivity (10^{-6} S/cm for tetragonal phase and 10^{-3} S/cm for cubic phase) but also good electrochemical stability against lithium (electrolyte window wider than 0 - 7 V) and excellent resistance to moisture [8, 9]. Since this garnet-type LLZO has shown nice performance as a solid electrolyte in the bulk form, it is expected to show satisfying properties as a thin film electrolyte. To the best of our knowledge, the LLZO electrolyte has only been synthesized as a bulk phase, with no research having been reported on LLZO thin films.

Given that LLZO is a complex oxide material, the preservation of stoichiometry from the target to the film would be very hard by conventional evaporation techniques. Therefore, a pulsed laser deposition system was employed. Utilizing highly energetic laser pulses, the target surface absorbs over 1 GW power and as a result all the elements are ablated at the same rate despite their usually different partial pressures in the vapor phase; thus the stoichiometry of the deposited film is more likely to be maintained. Considering that thin film batteries are fabricated at low temperatures, we explored the pulsed laser deposition of LLZO films at room temperature. The as-deposited films were annealed ex-situ for achieving better crystallinity. In this work, we are reporting the pulsed laser deposition of LLZO thin films at room temperature. The structural features, optical properties and electrical behavior of the as-deposited and post-annealed films were characterized and illustrated.

EXPERIMENTAL DETAILS

A high purity LLZO target was synthesized by a solution-based technique, which was described elsewhere. [10] A Li_2O target was prepared for compensation of lithium loss during laser deposition. For this purpose, high purity Li_2O powders were pressed into pellet and sintered at 750 °C for 8 hrs in flowing oxygen. Both of the targets were mounted on the target panel in the pulsed laser deposition (PLD) chamber. The target panel was rotated in a way that for every 100 shots of laser hitting on LLZO target, 10 shots of laser was directed onto Li_2O target. The KrF excimer laser (248 nm wavelength and 25 ns pulse width) was used in the PLD system. The total number of shots was 7,700; the laser frequency was 10 Hz and the energy fluence was $\sim 7.5 \text{ J/cm}^2$. A plasma plume was generated by the laser incident at 45°, and then deposited onto the substrates placed 4.5 cm away from the target. The background oxygen pressure was kept at 0.1 mbar. The films were annealed at different temperatures up to 1000 °C for 30 min at a ramp rate of 5 °C/min.

Single crystalline SrTiO_3 (STO) in the $\langle 100 \rangle$ orientation was used as one of the substrates in our experiment; it has a cubic structure similar to that of LLZO. The crystal structure and surface morphology of the films deposited on STO were characterized by X-ray diffraction (XRD) using $\text{CuK}\alpha$ radiation ($\lambda = 1.54 \text{ \AA}$) and scanning electron microscopy (SEM), respectively. The measurement of electrical properties was conducted from room temperature to 60 °C using the electrochemical impedance spectroscopy (EIS) function of a Gamry 600. For this, Pt was deposited on the surface of STO and Au was coated on top of the LLZO film, forming a Au/LLZO/Pt cell which was heated at 80 °C for 1 h to ensure good electrical contact. The structure of the cell is illustrated in Figure 1. Also, Sapphire $\langle 0001 \rangle$ was used as a substrate; and the reason for using sapphire is mentioned in the discussion section. The chemical composition of the films deposited on sapphire $\langle 0001 \rangle$ was analyzed by energy dispersive X-ray spectroscopy (EDS). The optical properties of the films were tested by UV-VIS spectrometer, in the wavelength range of 190 nm to 1100 nm.

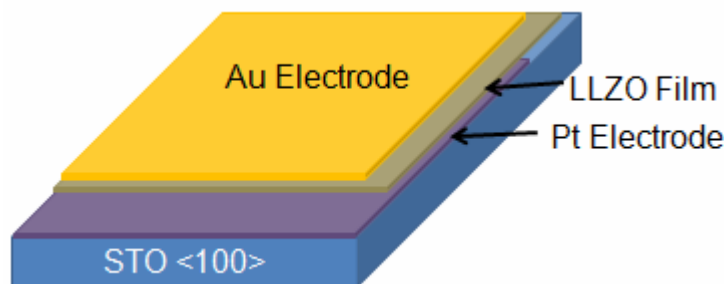


Figure 1. Schematic drawing of the Au/LLZO/Pt cell deposited on STO substrate

DISCUSSION

X-ray diffraction

Figure 2 shows the XRD patterns of the as-deposited and annealed films that were grown on STO $\langle 100 \rangle$ substrates. As can be seen, the as-deposited films were amorphous, showing no diffraction peak beside the ones for substrate. After annealing at 800 °C for 30 minutes, two broad peaks appeared around the 2θ values of 27.75° and 34.12°. Upon further annealing at 1000 °C for 30 minutes, these peaks became sharper and several more peaks appeared. We found that

these peaks correspond to the crystal orientations of cubic phase LLZO; and the peaks were labeled according to the JCPDS card (Reference code: 00-045-0109). Here it is important to note that in bulk LLZO system, the (420) peak is of the maximum intensity (100%) while (400) peak is only about 55%. However, in our films the strongest peak was (400), while (420) peak was only 15%. This indicates that our films may be slightly textured having a preferred orientation in the <100> direction. The fact that just the annealing of the as-deposited films resulted in crystalline LLZO films indicates that the as-deposited films were amorphous LLZO.

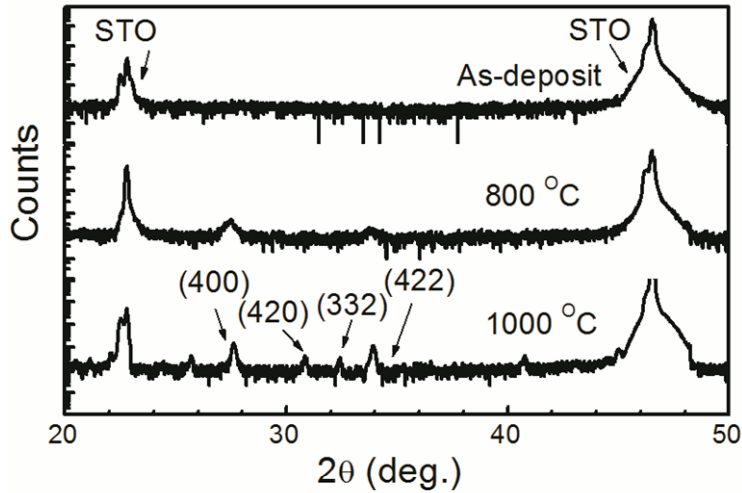


Figure 2. XRD patterns of the as deposited and annealed films.

Scanning electron microscopy

The SEM images of the as-deposited and annealed thin films on STO substrates are shown in Figure 3. The surface of the film deposited at room temperature (Figure 3a) was quite smooth with scattered dots which can be reduced by elongating the target-to-substrate distance. The surface of the film became less continuous after sintering at 1000 °C (Figure 3b), due to different thermal expansion coefficients between the film and the substrate. The thickness of the as-deposited film was revealed to be around 1 μm as seen from the cross-sectional image (Figure 3c).

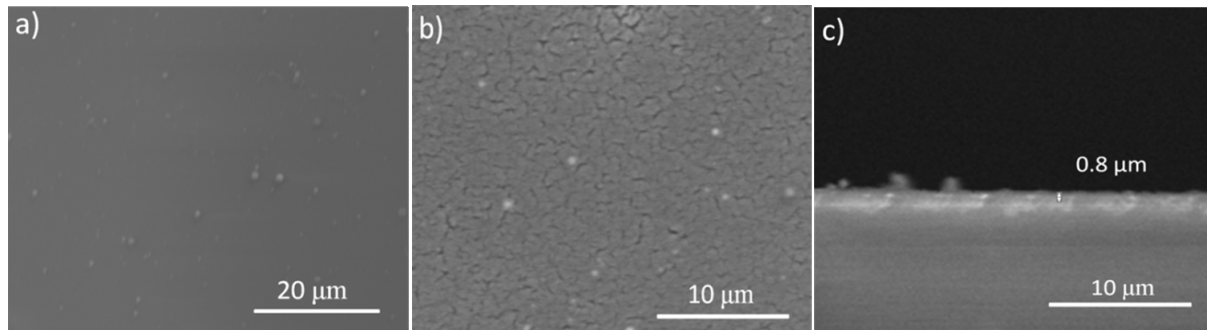


Figure 3. SEM images taken on the (a, b) surface and (c) cross section of the films.

In order to verify the chemical composition of the film, we conducted EDS measurements on the LLZO films grown on sapphire. The reason to choose sapphire as the substrate instead of STO is that the unique set of peaks for zirconium is overlapping that of strontium in their X-ray spectra. Figure 4 shows the EDS result for the cross-section of the as-deposited film. It was found that the counts for lanthanum and zirconium were close to the stoichiometric atomic ratio. The inset figure shows the counts of zirconium along the cross-section of the sample, from which we could confirm that the film thickness (marked by the gray bar) was around 1 μm .

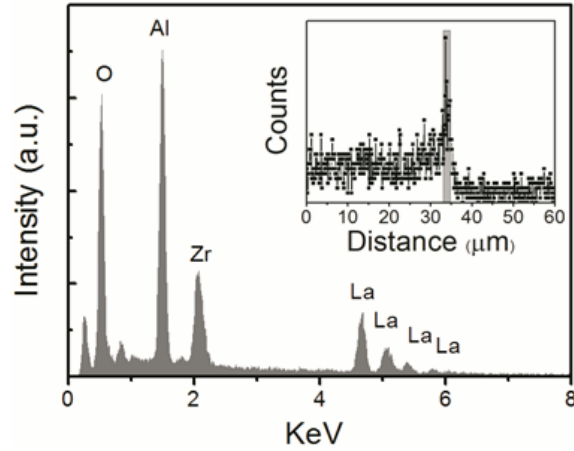


Figure 4. EDS spectrum of the LLZO films deposited on sapphire.

Optical transmission spectroscopy

The measurement of optical transmission properties can help us understand more about our films. The obtained optical transmission spectra of the as-deposited and annealed films are shown in Figure 5a. As you can see, the overall transmittance decreases for the annealed films in comparison to the as-deposited ones. This reduction is possibly due to the grain growth and defect formation in the films, also evidenced by the films shifting from transparent to opaque after annealing. It is shown that the transmission edge of the films shift to longer wavelengths after annealing, indicating a reduction of optical band gap E_g . E_g can be directly found out by fitting the absorption data with the following equation:

$$\alpha = A(h\nu - E_g)^n/h\nu \quad (1)$$

where α is the absorption coefficient, A is a constant, and $n = 1/2$ for direct band gap and 2 for indirect band gap materials [11]. The values of band gaps calculated by fitting the above equation are shown in Figure 4b. The linear behavior of the curve when $n = 1/2$ reveals the direct band-gap nature of the thin films. E_g is the intercept value when extrapolating the linear portion to the energy axis. For the first time, the optical band gap of the as-deposited LLZO thin film was found to be 5.13 eV, but decreased to 3.64 eV after annealing at 1000 °C.

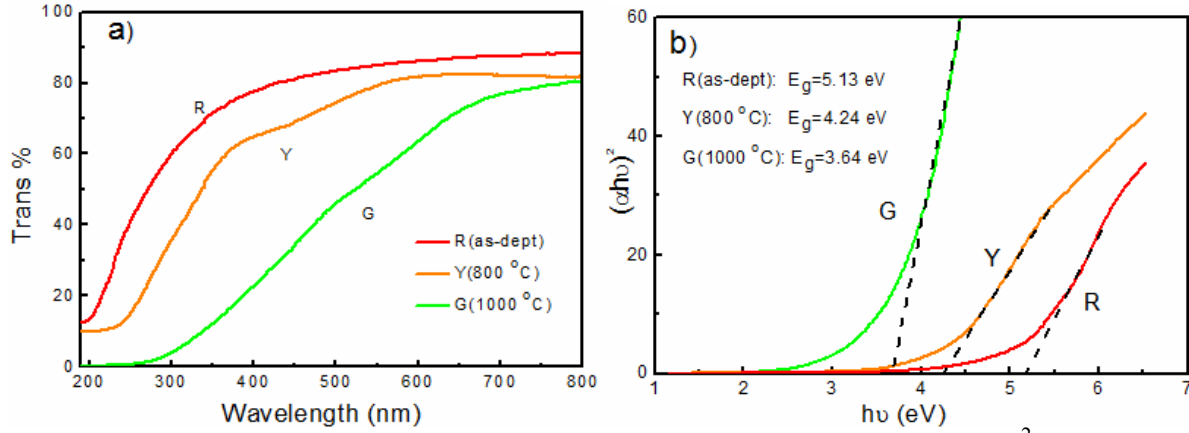


Figure 5. (a) Transmittance as a function of wavelength; (b) Plots of $(\alpha h\nu)^2$ as a function of photon energy ($h\nu$) for LLZO thin films.

Electrical properties

Electrical properties of the LLZO thin films were investigated for their potential application as solid-state electrolyte in lithium ion batteries. For this, a Au/LLZO/Pt/STO cell was fabricated as described in the experimental section. Figure 6 shows the Nyquist impedance plots of the as-deposited and annealed films, in the frequency range of 1 MHz to 100 Hz. The curve could be regarded to consist of a semicircle in the high frequency range and a tail in the low frequency range. The impedance data can be fitted by an equivalent circuit model drawn in the same figure, where R_{con} is the contact resistance, R_{el} is the electrolyte resistance, Q is the constant phase element, and Z_w is the Warburg impedance. By fitting the equivalent circuit model to the data while including dimensional parameters, we obtained an ionic conductivity value of 3.35×10^{-7} S/cm for the as-deposited films. This value is even better than the total ionic conductivity of the tetragonal LLZO bulk samples [12]. The activation energy of the films was estimated to be 0.36 eV. After annealing the films at 800 °C for 30 min, the ionic conductivity of the sample decreased to 1.78×10^{-7} S/cm, almost half that of the as-deposited films. This is possibly due to the increased hardness for ionic transport through the films that were full of defects and cracks during crystallization.

It is notable that we choose 800 °C as the annealing temperature, since the crystallization of the films into cubic phase was not obvious even at 600 °C. The annealed films without forming the highly conductive cubic phase should have a lower ionic conductivity than the as-deposited ones due to the lower quality of the films annealed at several hundred degrees Celsius. Therefore, we choose to measure the ionic conductivity of the films annealed at 800 °C, at which the highly conductive cubic phase was formed. However, the film still showed lower ionic conductivity than the as-deposited ones, which demonstrated that the formation of the cubic phase has only a minor effect on the transport property of the films.

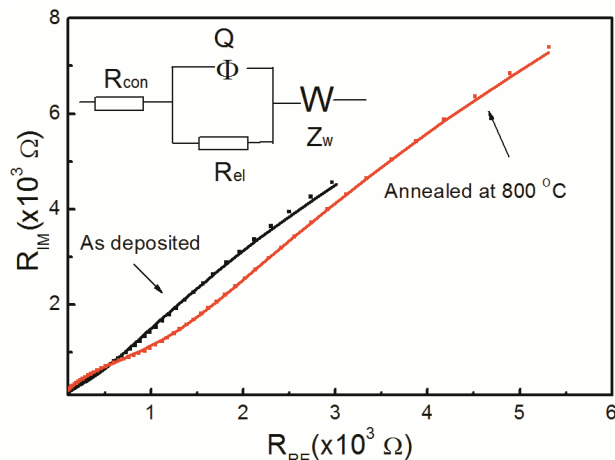


Figure 6. Nyquist plots of the complex impedance for LLZO films.

CONCLUSIONS

We have successfully fabricated LLZO thin films through pulsed laser deposition technique at room temperature. The as-deposited films were amorphous and then crystallized after annealing. With the increase of annealing temperature, the optical band gap red-shifted from the original value of 5.13 eV down to 3.64 eV. The as-deposited films exhibited an ionic conductivity of 3.35×10^{-7} S/cm at room temperature with an activation energy of 0.36 eV. In all, the LLZO thin films are a very promising solid-state electrolyte for realizing next generation TFBs.

REFERENCES

1. C. Wang, L. Taherabadi, G. Jia, M. Madou, Y. Yeh and B. Dunn, *Electrochem. Solid-State Lett.* **7**, A45 (2004).
2. R.W. Hart, H. S. White, B. Dunn and D.R. Rolison, *Electrochem. Commun.* **5** (2), 120 (2003).
3. S.D. Jones and J.R. Akridge, *J. Power Sources* **54**, 63 (1995).
4. N.A. Kyeremateng, F. Dumur, P. Knauth, B. Pecquenard and T. Djenizian, *Electrochem. Commun.* **13**, 894 (2011).
5. H. Xia, H.L. Wang, W. Xiao, M.O. Lai and L. Lu, *Int. J. Surf. Sci. Eng.* **3**, 23 (2009).
6. J. B. Goodenough, *Solid State Microbatteries* (Plenum Press, New York, 1990), pp. 174.
7. W.C. West, J.F. Whitacre and J.R. Lim, *J. Power Sources* **126**, 134 (2004).
8. R. Murugan, V. Thangadurai and W. Weppner, *Angew. Chem. Int. Ed.* **46**, 7778 (2007).
9. Pdf S. Ohta, T. Kobayashi, J. Seki and T. Asaoka, *J. Power Source* **202**, 332 (2012).
10. J. Tan and A. Tiwari, *Electrochem. Solid-State Lett.* **15**, A37 (2012).
11. F.I Ezema and R.U. Osuji, *Chalcogenide Lett.* **4**, 69 (2007).
12. J. Awaka, N. Kijima, H. Hayakawa and J. Akimoto, *J. Solid State Chem.* **182**, 2046 (2009).